June 11, 1891.

Sir WILLIAM THOMSON, D.C.L., LL.D., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

Sir John Conroy, Mr. Edwin Bailey Elliott, Mr. Percy C. Gilchrist, Dr. William Dobinson Halliburton, Mr. John Edward Marr, Mr. Ludwig Mond, Professor Silvanus Phillips Thompson, and Captain Thomas Henry Tizard were admitted into the Society.

The following Papers were read:—

I. "On Some Test Cases for the Maxwell-Boltzmann Doctrine regarding Distribution of Energy." By Sir William Thomson, D.C.L., P.R.S. Received June 11, 1891.

1. Maxwell, in his article ('Phil. Mag.,' 1860) "On the Collision of Elastic Spheres," enunciates a very remarkable theorem, of primary importance in the kinetic theory of gases, to the effect that, in an assemblage of large numbers of mutually colliding spheres of two or of several different magnitudes, the mean kinetic energy is the same for equal numbers of the spheres irrespectively of their masses and diameters; or, in other words, the time-averages of the squares of the velocities of individual spheres are inversely as their masses. The mathematical investigation given as a proof of this theorem in that first article on the subject is quite unsatisfactory; but the mere enunciation of it, even if without proof, was a very valuable contribution to science. In a subsequent paper ("Dynamical Theory of Gases," 'Phil. Trans.' for May, 1866) Maxwell finds in his equation (34) ('Collected Works,' p. 47), as a result of a thorough mathematical investigation, the same theorem extended to include collisions between Boscovich points with mutual forces according to any law of distance, provided only that not more than two points are in collision (that is to say, within the distances of their mutual influence) simultaneously. Tait confirms Maxwell's original theorem for colliding spheres of different magnitudes in an interesting and important examination of the subject in §§ 19, 20, 21 of his paper "On the Foundations of the Kinetic Theory of Gases" ('Trans. R.S.E.' for May, 1866).

2. Boltzmann, in his "Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten" ('Sitzb. K.

Akad. Wien,' October 8, 1868), enunciated a large extension of this theorem, and Maxwell a still wider generalisation in his paper "On Boltzmann's Theorem on the Average Distribution of Energy in a System of Material Points" ('Cambridge Phil. Soc. Trans.,' May 6, 1878, republished in vol. 2 of Maxwell's 'Scientific Papers,' pp. 713—741), to the following effect (p. 716):—

"In the ultimate state of the system, the average kinetic energy of two given portions of the system must be in the ratio of the number of degrees of freedom of those portions."

Much disbelief and doubt has been felt as to the complete truth, or the extent of cases for which there is truth, of this proposition.

3. For a test case, differing as little as possible from Maxwell's original case of solid elastic spheres, consider a hollow spherical shell and a solid sphere—globule we shall call it for brevity—within the shell. I must first digress to remark that what has hitherto by Maxwell and Clausius and others before and after them been called for brevity an "elastic sphere," is not an elastic solid, capable of rotation and of elastic deformation; and therefore capable of an infinite number of modes of steady vibration, into which, of finer and finer degrees of nodal sub-division and shorter and shorter periods, all translational energy would, if the Boltzmann-Maxwell generalised proposition were true, be ultimately transformed by collisions. The "smooth elastic spheres" are really Boscovich point-atoms, with their translational inertia, and with, for law of force, zero force at every distance between two points exceeding the sum of the radii of the two balls, and infinite repulsion at exactly this distance. We may use Boscovich similarly for the hollow shell with globule in its interior, and so do away with all question as to vibrations due to elasticity of material, whether of the shell or of the globule. Let us simply suppose the mutual action between the shell and the globule to be nothing except at an instant of collision, and then to be such that their relative component velocity along the radius through the point of contact is reversed by the collision, while the motion of their centre of inertia remains unchanged.

4. For brevity, we shall call the shell and interior globule of § 3, a double molecule, or sometimes, for more brevity, a doublet. The "smooth elastic sphere" of § 3 will be called simply an atom, or a single atom; and the radius or diameter or surface of the atom will mean the radius or diameter or surface of the corresponding sphere. (This explanation is necessary to avoid an ambiguity which might occur with reference to the common expression "sphere of action" of a Boscovich atom.)

5. Consider now a vast number of atoms and doublets, enclosed in a perfectly rigid fixed surface, having the property of reversing the normal component velocity of approach of any atom or shell or doublet

at the instant of contact of surfaces, while leaving unchanged the absolute velocity of the centre of inertia of the two. Let any velocity or velocities in any direction or directions be given to any one or more of the atoms or of the shells or globules constituting the doublets. According to the Boltzmann-Maxwell doctrine, the motion will become distributed through the system, so that ultimately the time-average kinetic energy of each atom, each shell, and each globule shall be equal; and therefore that of each doublet double that of each atom. This is certainly a very marvellous conclusion; but I see no reason to doubt it on that account. After all, it is not obviously more marvellous than the seemingly well proved conclusion, that in a mixed assemblage of colliding single atoms, some of which have a million million times the mass of others, the smaller masses will ultimately average a million times the velocity of the larger. But it is not included in Maxwell's proof for single atoms of different masses [(34) of his "Dynamical Theory of Gases" referred to above]; and the condition that the globules enclosed in the shells are prevented by the shells from collisions with one another violates Tait's condition [(C) of § 18 of "Foundations of K.T. Gases"], "that there is perfectly free access for collision between each pair of particles whether of the same or of different systems." An independent investigation of such a simple and definite case as that of the atoms and doublets defined in §§ 3—5 is desirable as a test, or would be interesting as an illustration were test not needed, for the exceedingly wide generalisation set forth in the Boltzmann-Maxwell doctrine.

6. Next, instead of only a single globule within the shell of § 4, let there be a vast number. To fix ideas let the mass of the shell be equal to a hundred times the sum of the masses of the globules, and let the number of the globules be a hundred million million. Let two such shells be connected by a push-and-pull massless spring. Let all be given at rest, with the spring stretched to any extent; and then left free. According to the Boltzmann-Maxwell doctrine, the motion produced initially by the spring will become distributed through the system, so that ultimately the sum of the kinetic energies of the globules within each shell will be a hundred million million times the average kinetic energy of the shell. The average velocity* of the shell will ultimately be a hundred-millionth of the average velocity of the globules. A corresponding proposition in the kinetic theory of gases is that, if two rigid shells each weighing 1 gram, and containing a centigram of monatomic gas, be attached to the two prongs of a massless perfectly elastic tuning fork, and set to vibrate, the gas will become heated in virtue of its viscous resistance

* The "average velocity of a particle," irrespectively of direction, is (in the kinetic theory of gases) a convenient expression for the square root of the time-average of the square of its velocity.

to the vibration excited in it by the vibration of the shell, until nearly all the initial energy of the tuning fork is thus spent.

7. Going back to the double molecules of § 5, suppose the internal globule to be so connected by massless springs with the shell that the globule is urged towards the centre of the shell with a force simply proportional to the distance between the centres of the two. This arrangement, which I gave in my Baltimore Lectures, in 1884, as an illustration for vibratory molecules embedded in ether, would be equivalent to two masses connected by a massless spring, if we had only motions in one line to consider; but it has the advantage of being perfectly isotropic, and giving for all motions parallel to any fixed line exactly the same result as if there were no motion perpendicular to it. When a pair of masses connected by a spring strikes a fixed obstacle or a movable body, with the line of their centres not exactly perpendicular to the tangent plane of contact, it is caused to rotate. No such complication affects our isotropic doublet. An assemblage of such doublets being given moving about within a rigid enclosing surface, will the ultimate statistics be, for each doublet,* equal average kinetic energies of motion of centre of inertia, and of relative motion of the two constituents?

* This implies equal average kinetic energies of the two constituents; and, conversely, equal average kinetic energies of the two constituents, except in the case of their masses being equal, implies the equality stated in the text. Let u, u' be absolute component velocities of two masses, m, m', perpendicular to a fixed plane; U the corresponding component velocity of their centre of inertia; and r that of their mutual relative motion. We have

$$u = \mathrm{U} - \frac{m'r}{m+m'}, \qquad u' = \mathrm{U} + \frac{mr}{m+m'}, \quad \ldots\ldots\ldots\ldots \quad (1);$$

whence
$$mu^2 - m'u'^2 = (m-m')\left[\mathrm{U}^2 - \frac{mm'r^2}{(m+m')^2}\right] - \frac{4mm'}{m+m'}\mathrm{U}r \quad \ldots\ldots\ldots \quad (2).$$

Now suppose the time-average of Ur to be zero. In every case in which this is so we have, by (2),

$$\text{Time-av.}\left\{mu^2 - m'u'^2\right\} = (m-m') \times \text{Time-av.}\left\{\mathrm{U}^2 - \frac{mm'r^2}{(m+m')^2}\right\} \quad \ldots\ldots \quad (3).$$

Hence in any case in which

$$\text{Time-av. } mu^2 = \text{Time-av. } m'u'^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

we have
$$(m-m') \times \text{Time-av.}\left\{\mathrm{U}^2 - \frac{mm'r^2}{(m+m')^2}\right\} = 0 \quad \ldots\ldots\ldots\ldots \quad (5),$$

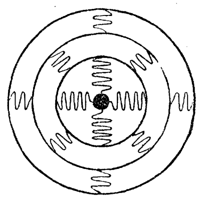
and therefore, except when $m = m'$, we must have

$$\text{Time-av. } (m+m')\,\mathrm{U}^2 = \text{Time-av.} \frac{mm'r^2}{m+m'} \quad \ldots\ldots\ldots\ldots\ldots \quad (6),$$

which proves the proposition, because, as we readily see from (1), $\frac{1}{2}mm'r^2/(m+m')$ is, in every case, the kinetic energy of the relative motions, $u - \mathrm{U}$, and $\mathrm{U} - u'$.

8. If we try to answer this question synthetically, we find a complex and troublesome problem in the details of all but the very simplest case of collision which can occur, which is direct collision between two not previously vibrating doublets, or any collision of one not previously vibrating doublet against a fixed plane. In this case, if the masses of globule and shell are equal, a complete collision consists of two impacts at an interval of time equal to half the period of free vibration of the doublet, and after the second impact there is separation without vibration, just as if we had had single spheres instead of the doublets. But in oblique collision between two not previously vibrating doublets, even if the masses of shell and globule are equal, we have a somewhat troublesome problem to find the interval between the two impacts, *when there are two*, and to find the final resulting vibration. When the component relative motion parallel to the tangent plane of the first impact exceeds a certain value depending on the radius of the outer surface of the shell, the period of free vibration of the doublets, and the relative velocity of approach; there is no second impact, and the doublets separate with no relative velocity perpendicular to the tangent plane, but each with the energy of that component of its previous motion converted into vibrational energy. When the mass of the shell is much smaller than the mass of the interior globule, almost every collision will consist of a large number of impacts. It seems exceedingly difficult to find how to calculate true statistics of these chattering collisions, and arrive at sound conclusions as to the ultimate distribution of energy in any of the very simplest cases other than Maxwell's original case of 1860; but, if the Boltzmann-Maxwell generalised doctrine is true, we ought to be able to see its truth as essential, with special clearness in the simplest cases, even without going through the full problem presented by the details. I can find nothing in Maxwell's latest article on the subject ('Camb. Phil. Trans.,' May 6, 1878), or in any of his previous papers, proving an affirmative answer to the question of § 7.

9. Going back to § 6, let the globules be initially distributed as nearly as may be homogeneously through the hollow; let each globule be connected with neighbours by massless springs; and let all the globules which are near the inner surface of the shell be connected with it also by massless springs. Or let any number of smaller shells be enclosed within our outer shell, and connected by massless springs as represented by the accompanying diagram, taken from a reprint of my Baltimore lectures now in progress. Let two such outer shells, given at rest with their systems of globules in equilibrium within them, be connected by massless springs, and be started in motion, as were the shells of § 6. There will not now be the great loss of energy from the vibration of the shells which there was in § 6. On the contrary, the ultimate average kinetic energy of the



whole two hundred million million globules will be certainly small in comparison with the ultimate average kinetic energy of the single shell. It may be because each globule of § 6 is free to wander that the energy is lost from the shell in that case, and distributed among them. There is nothing vague in their motion allowing them to take more and more energy, now when they are connected by the massless springs. If we suppose the motions infinitesimal, or if, whatever their ranges may be, all forces are in simple proportion to displacements, the elementary dynamical theorem of *fundamental modes* shows how to find determinately each of the 600 million million and six simple harmonic vibrations of which the motion resulting from the prescribed initial circumstances is constituted. It tells us that the sum of the potential and kinetic energies of each mode remains always of constant value, and that the time-average of the changing kinetic energy during its period is half of this constant value. Without fully solving the problem for the 600 million million and six co-ordinates, it is easy to see that the gravest fundamental mode of the motion actually produced in the prescribed circumstances differs but little in period and energy from the single simple harmonic vibration which the two shells would take if the globules were rigidly connected to them, or were removed from within them, and the other initial circumstances were those of § 6. But this conclusion depends on the forces being *rigorously* in simple proportion to displacements.

10.* In no real case could they be so, and if there is any deviation from the simple proportionality of force to displacement, the independent superposition of motions does not hold good. We have still a theorem of fundamental modes, although, so far as I know, this theory has not yet been investigated.† For any stable system moving with a given sum, E, of potential and kinetic energies, there must in general be *at least as many fundamental modes of rigorously periodic motion as there are freedoms* (or independent variables). But the configuration of each fundamental mode is now not *generally* similar

* Sections 10 to 17 added July 10, 1891.

† It is similar for *adynamic* cases, that is to say, cases in which there is no potential energy, as, for example, a particle constrained to remain on a surface and moving along a geodetic line under the influence of no "applied" force.

for different values of E; and superposition of different fundamental modes, whether with the same or with different values of E, *has now no meaning*. It seems to me probable that every fundamental mode is essentially unstable. It is so if Maxwell's fundamental assumption* "that the system if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy" is true. It seems to me quite probable that this assumption *is* true, provided the "actual state of motion" is not exactly, as to position and velocity, a configuration of some one of the fundamental modes of rigorously periodic motion, and provided also that the "system" has not any exceptional character, such as those indicated by Maxwell for cases in which he warns† us that his assumption does not hold good.

11. But, conceding Maxwell's fundamental assumption, I do not see in the mathematical workings of his paper‡ any proof of his conclusion "that the average kinetic energy corresponding to any one of the variables is the same for every one of the variables of the system." Indeed, as a general proposition its meaning is not explained, and seems to me inexplicable. The reduction of the kinetic energy to a sum of squares§ leaves the several parts of the whole with no correspondence to any defined or definable set of independent variables. What, for example, can the meaning of the conclusion|| be for the case of a jointed pendulum? (a system of two rigid bodies, one supported on a fixed, horizontal axis and the other on a parallel axis fixed relatively to the first body, and both acted on only by gravity). The conclusion is quite intelligible, however (but is it true?), when the kinetic energy is expressible as a sum of squares of rates of change of single co-ordinates each multiplied by a function of all, or of some, of the co-ordinates.¶ Consider, for example, the still easier case of these coefficients constant.

12. Consider more particularly the easiest case of all, motion of a single particle in a plane, that is the case of just two independent variables, say, x, y; and kinetic energy equal to $\frac{1}{2}(\dot{x}^2+\dot{y}^2)$. The equations of motion are

$$\frac{d^2x}{dt^2} = -\frac{dV}{dx}, \qquad \frac{d^2y}{dt^2} = -\frac{dV}{dy},$$

* "Scientific Papers," Vol. II, p. 714.

† *Ibid.*, pp. 714, 715.

‡ *Ibid.*, pp. 716—726.

§ *Ibid.*, p. 722.

|| Or of Maxwell's "$\dot{b}$," in p. 723.

¶ [It may be untrue for one set of co-ordinates, though true for others. Consider, for example, uniform motion in a circle. For all systems of rectilineal rectangular co-ordinates (x, y), time-av. $\dot{x}^2$ = time-av. $\dot{y}^2$; but for polar co-ordinates (r, θ) we have *not* time-av. $\dot{r}^2$ equal to time-av. $r^2\dot{\theta}^2$.—W. T., July 21, 1891.]

where V is the potential energy, which may be any function of x, y, subject only to the condition (required for stability) that it is essentially positive (its least value being, for brevity, taken as zero). It is easily proved that, with any given value, E, for the sum of kinetic and potential energies there are two determinate modes of periodic motion; that is to say, there are two finite closed curves such that if m be projected from any point of either with velocity equal to $\sqrt{[2(E-V)]}$ in the direction, eitherwards, of the tangent to the curve, its path will be exactly that curve. In a very special class of cases there are only two such periodic motions, but it is obvious that there are more than two in other cases.

13. Take, for example,

$$V = \tfrac{1}{2}(\alpha^2x^2+\beta^2y^2+cx^2y^2).$$

For all values of E we have

$$\left.\begin{array}{l} x = a\cos(\alpha t-e) \\ y = 0 \end{array}\right\} \text{ and } \left.\begin{array}{l} y = 0 \\ x = b\cos(\beta t-f) \end{array}\right\}$$

as two fundamental modes. When E is infinitely small we have only these two; but for any finite value of E we have clearly an infinite number of fundamental modes, and *every mode* differs infinitely little from being a fundamental mode. To see this let m be projected from any point N in OX, in a direction perpendicular to OX, with a velocity equal to $\sqrt{(2E-\alpha^2ON^2)}$. After a sufficiently great number of crossings and re-crossings across the line X′OX, the particle will cross this line very nearly at right angles, at some point, N′. Vary the position of N very slightly in one direction or other, and re-project m from it perpendicularly and with proper velocity; till (by proper "trial and error" method) a path is found, which, after still the same number of crossings and re-crossings, crosses exactly at right angles at a point N″, very near the point N′. Let m continue its journey along this path and, after just as many more crossings and re-crossings, it will return *exactly* to N, and cross OX there, *exactly* at right angles. Thus the path from N to N″ is exactly half an orbit, and from N″ to N the remaining half.

14. When $cE/(\alpha^2\beta^2)$ is a small numeric, the part of the kinetic energy expressed by $\frac{1}{2}cx^2y^2$ is very small in comparison with the total energy, E. Hence the path is at every time very nearly the resultant of the two primary fundamental modes formulated in § 13; and an interesting problem is presented, to find (by the method of the "variation of parameters") a, e, b, f, slowly varying functions of t, such that

$$x = a\ \sin(\alpha t-e), \qquad y = b\ \sin(\beta t-f),$$

$$\dot{x} = a\alpha\cos(\alpha t-e), \qquad \dot{y} = b\beta\cos(\beta t-f),$$

shall be the rigorous solution, or a practical approximation to it. Careful consideration of possibilities in respect to this case [$c\text{E}/(\alpha^2\beta^2)$ very small] seem thoroughly to confirm Maxwell's fundamental assumption quoted in § 11; and that it is correct whether $c\text{E}/(\alpha^2\beta^2)$ be small or large seems exceedingly probable, or quite certain.

15. But it seems also probable that Maxwell's *conclusion*, which for the case of a material point moving in a plane is

$$\text{Time-av. } \dot{x}^2 = \text{Time-av. } \dot{y}^2 \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

is not true when α^2 differs from β^2. It is certainly not proved. No dynamical principle except the equation of energy,

$$\tfrac{1}{2}(\dot{x}^2+\dot{y}^2) = \text{E}-\text{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2),$$

is brought into the mathematical work of pp. 722—725, which is given by Maxwell as proof for it. Hence any arbitrarily drawn curve might be assumed for the path without violating the dynamics which enters into Maxwell's investigation; and we may draw curves for the path such as to satisfy (1), and curves not satisfying (1), but all traversing the whole space within the bounding curve

$$\tfrac{1}{2}(\alpha^2x^2+\beta^2y^2+cx^2y^2) = \text{E} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3),$$

and all satisfying Maxwell's fundamental assumption (§ 11).

16. The meaning of the question is illustrated by reducing it to a purely geometrical question regarding the path, thus:—calling θ the inclination to x of the tangent to the path at any point xy, and q the velocity in the path, we have

$$\dot{x} = q\cos\theta, \qquad \dot{y} = q\sin\theta \quad \ldots\ldots\ldots\ldots \quad (4),$$

and therefore, by (2) $\quad q = \sqrt{\{2(\text{E}-\text{V})\}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5).$

Hence, if we call s the total length of curve travelled,

$$\int \dot{x}^2 dt = \int q\cos^2\theta\, q\,dt = \int \sqrt{\{2(\text{E}-\text{V})\}}\cos^2\theta\, ds \ldots\ldots \quad (6);$$

and the question of § 15 becomes, Is or is not

$$\frac{1}{\text{S}}\int_0^{\text{S}} ds\sqrt{\{2(\text{E}-\text{V})\}}\cos^2\theta = \frac{1}{\text{S}}\int_0^{\text{S}} ds\sqrt{\{2(\text{E}-\text{V})\}}\sin^2\theta\,? \;\ldots \quad (7),$$

where S denotes so great a length of path that it has passed a great number of times very near to every point within the boundary (3), very nearly in every direction.

17. Consider now separately the parts of the two members of (7) derived from portions of the path which cross an infinitesimal area $d\sigma$ having its centre at (x, y). They are respectively

$$\surd\{2(E-V)\}\, d\sigma\int_0^\pi N d\theta\cos^2\theta, \quad \text{and} \quad \surd\{2(E-V)\}\, d\sigma\int_0^\pi N d\theta\sin^2\theta \quad \ldots\ldots (8),$$

where $Nd\theta$ denotes the number of portions of the path, per unit distance in the direction inclined $\frac{1}{2}\pi+\theta$ to x, which pass eitherwards across the area in directions inclined to x at angles between the values $\theta-\frac{1}{2}d\theta$ and $\theta+\frac{1}{2}d\theta$. The most general possible expression for N is, according to Fourier,

$$\left.\begin{aligned} N = A_0 + A_1\cos 2\theta + A_2\cos 4\theta + \&c. \\ + B_1\sin 2\theta + B_2\sin 4\theta + \&c. \end{aligned}\right\} \quad \ldots\ldots\ldots (9).$$

Hence the two members of (8) become respectively

$$\surd\{2(E-V)\}\, d\sigma\,\tfrac{1}{2}\pi(A_0+\tfrac{1}{2}A_1), \quad \text{and} \quad \surd\{2(E-V)\}\, d\sigma\,\tfrac{1}{2}\pi(A_0-\tfrac{1}{2}A_1) \quad \ldots\ldots\ldots (10).$$

Remarking that A_0 and A_1 are functions of x, y, and taking $d\sigma = dxdy$, we find, from (10), for the two totals of (7) respectively

$$\left.\begin{aligned} &\tfrac{1}{2}\pi\iint dx\,dy(A_0+\tfrac{1}{2}A_1)\surd[2(E-V)] \\ \text{and} \quad &\tfrac{1}{2}\pi\iint dx\,dy(A_0-\tfrac{1}{2}A_1)\surd[2(E-V)] \end{aligned}\right\} \quad \ldots\ldots\ldots (11),$$

where $\iint dxdy$ denotes integration over the whole space enclosed by (3). These quantities are equal if and only if $\iint dx\,dy\,A_1$ vanishes; it does so, clearly, if $\alpha=\beta$; but it seems improbable that, except when $\alpha=\beta$, it can vanish generally; and unless it does so, our present test case would disprove the Boltzmann-Maxwell general doctrine.

II. "On Electrical Evaporation." By William Crookes, F.R.S.

Received June 4, 1891.

It is well known that when a vacuum tube is furnished with internal platinum electrodes, the adjacent glass, especially near the negative pole, speedily becomes blackened, owing to the deposition of metallic platinum. The passage of the induction current greatly stimulates the motion of the residual gaseous molecules; those condensed upon and in the immediate neighbourhood of the negative pole are shot away at an immense speed in almost straight lines, the speed varying with the degree of exhaustion and with the intensity of the induced current. Platinum being used for the negative pole,